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Evaluating the electronic and vibrational contributions to second and third harmonic scattering responses

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Introduction and objectives

The interaction between an electric field (\vec{E}) and a molecular system induces a dipole moment, through reorganization of the electron cloud (**electronic** contribution) and of the nuclei (**vibrational** contribution):

$$\Delta\vec{\mu}(\vec{E}) = \alpha \cdot \vec{E} + \frac{1}{2!} \beta : \vec{E}^2 + \frac{1}{3!} \gamma : \vec{E}^3 + \dots$$

where α is the polarizability (rank 2 tensor) and β , γ are the first and second hyperpolarizabilities (rank 3 and 4 tensors). The experiments rely on relative rather than absolute measurements, which requires precise knowledge of the response of these reference compounds.

The goals of this work^{1,2} are:

- The definition of reference values. Here, a model system, the **water** molecule, will be considered;
- The definition of an appropriate level of approximation since it is the first quantum chemistry investigations on γ_{THS} ;
- To assess the impact of vibrational contributions.

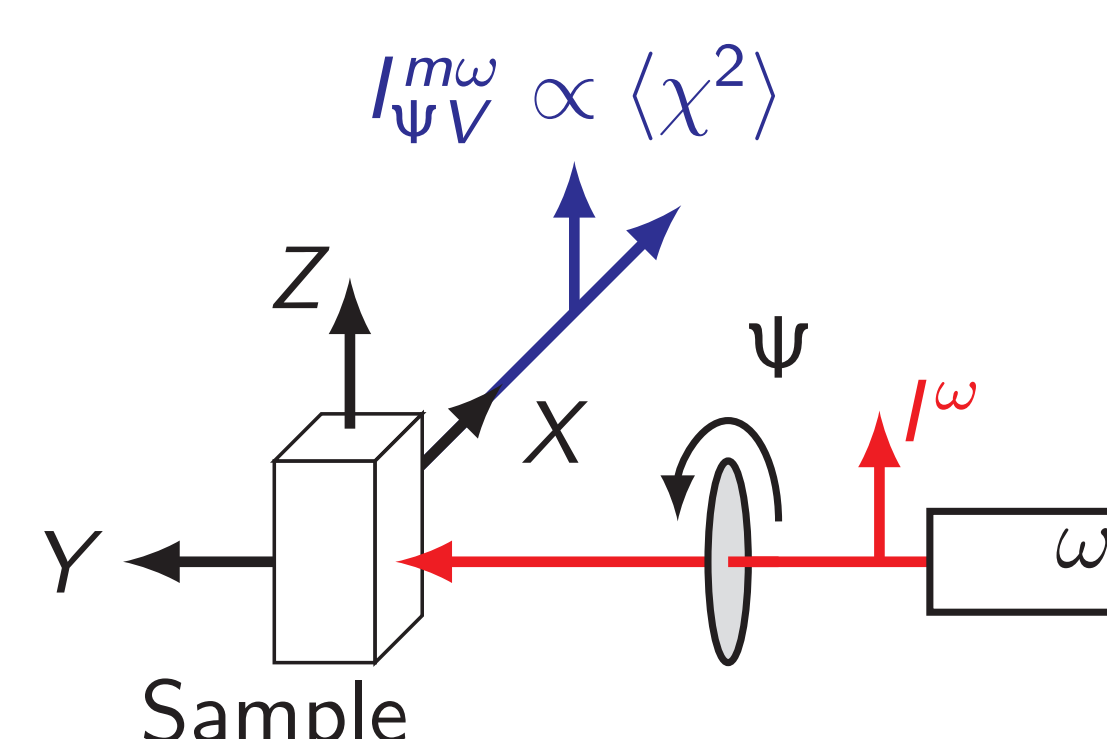
Computational details

Gas phase geometries and hyperpolarizabilities computed with Dalton 2016, with a hierarchy of coupled cluster methods (CCS, CC2, CCSD), in combination with quadratic/cubic response functions⁴ and the (d-)aug-cc-pVXZ (X=D, T) family to check the impact of the basis set.

A homemade code (NACHOS) was developed to perform numerical differentiation in order to carry out vibrational contributions.



SHS and THS measurements



Geometry	$\langle \chi^2 \rangle$	
	$m=2$	$m=3$
$I_{VV} (\Psi = \pi/2)$	$\langle \beta_{ZZZ}^2 \rangle$	$\langle \gamma_{ZZZZ}^2 \rangle$
$I_{HV} (\Psi = 0)$	$\langle \beta_{ZXX}^2 \rangle$	$\langle \gamma_{ZXXX}^2 \rangle$

For a non-polarized incident signal, in the laboratory frame,³

$$\left. \begin{aligned} \beta_{SHS} &= \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZXX}^2 \rangle} \\ \gamma_{THS} &= \sqrt{\langle \gamma_{ZZZZ}^2 \rangle + \langle \gamma_{ZXXX}^2 \rangle} \end{aligned} \right\} DR = \frac{I_{VV}}{I_{HV}}.$$

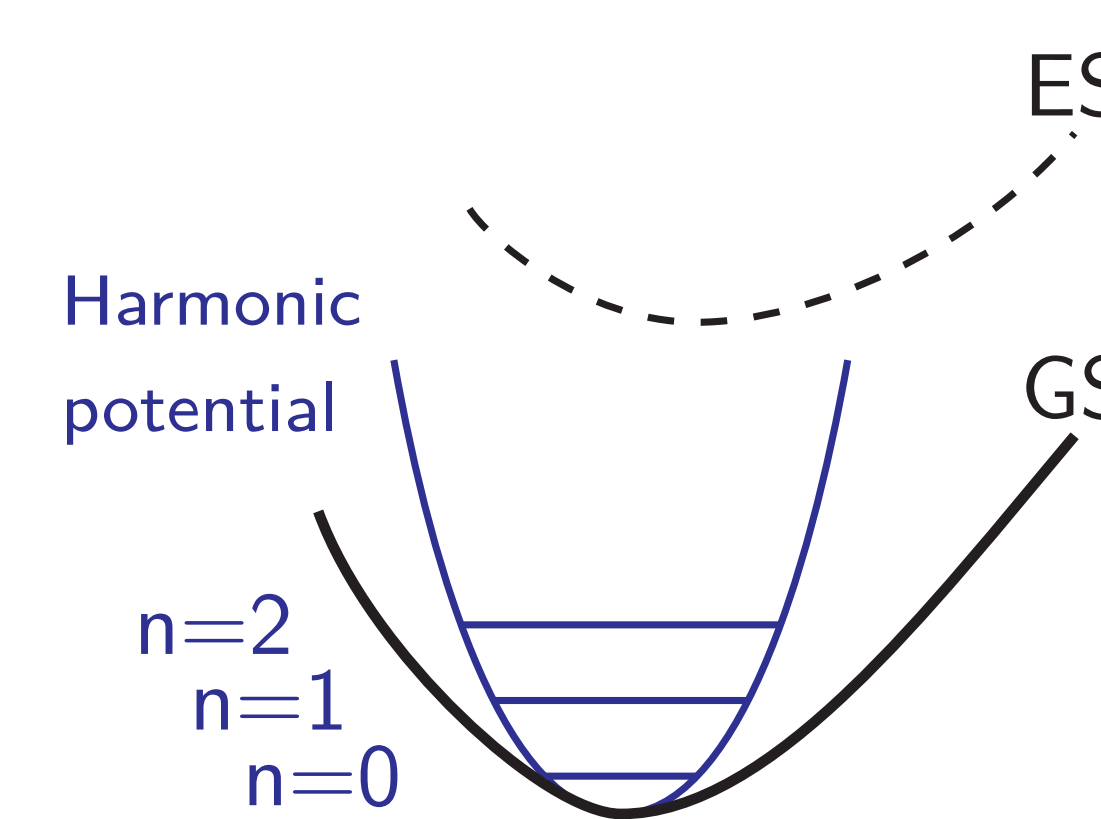
The depolarization ratio (DR) is linked to the geometry of the NLOphore.¹

Vibrational contributions

In the frozen nuclei approximation, the vibrational contributions are missing. They are divided in two parts, **ZPVA** and **pv**, which requires different geometrical derivatives of molecular properties w.r.t. normal modes, up to **second order**.⁵

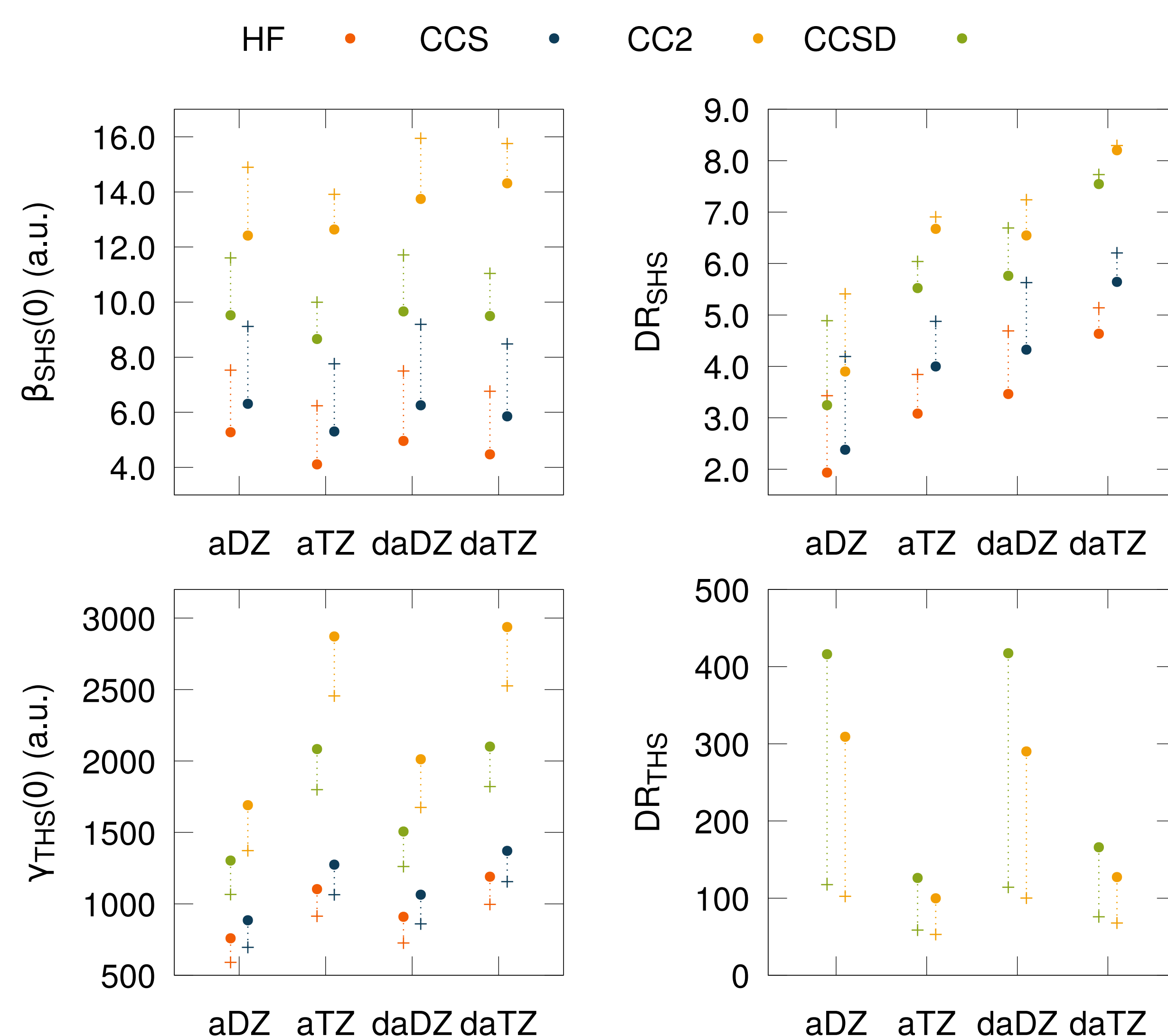
$$\Delta P^{ZPVA} = [P]^I, \beta^{pv} = [\mu\alpha]^0 + [\mu^3]^I + [\mu\alpha]^{II},$$

$$\gamma^{pv} = [\alpha^2]^0 + [\mu\beta]^0 + [\mu^2\alpha]^I + [\alpha^2]^{II} + [\mu\beta]^{II} + [\mu^4]^{II}.$$



Results

- Impact of the basis set and of the method on the static first and second hyperpolarizabilities of water. The electronic value is marked with a cross, while the total (electronic+vibrational) is marked with plain circles:



Substantial electron correlation and basis sets effects are evidenced (especially for DR_{THS}). The CCSD/d-aug-cc-pVTZ level is mandatory to study for investigating the impact of vibrational contribution for water. For the electronic part, it is in excellent agreement with calculation at the CCSD/d-aug-cc-pV5Z level.¹

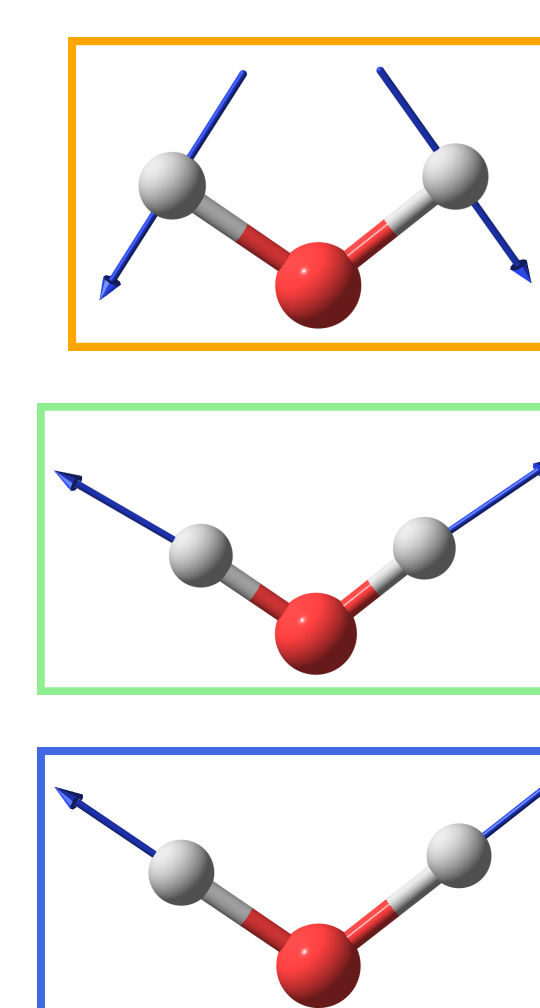
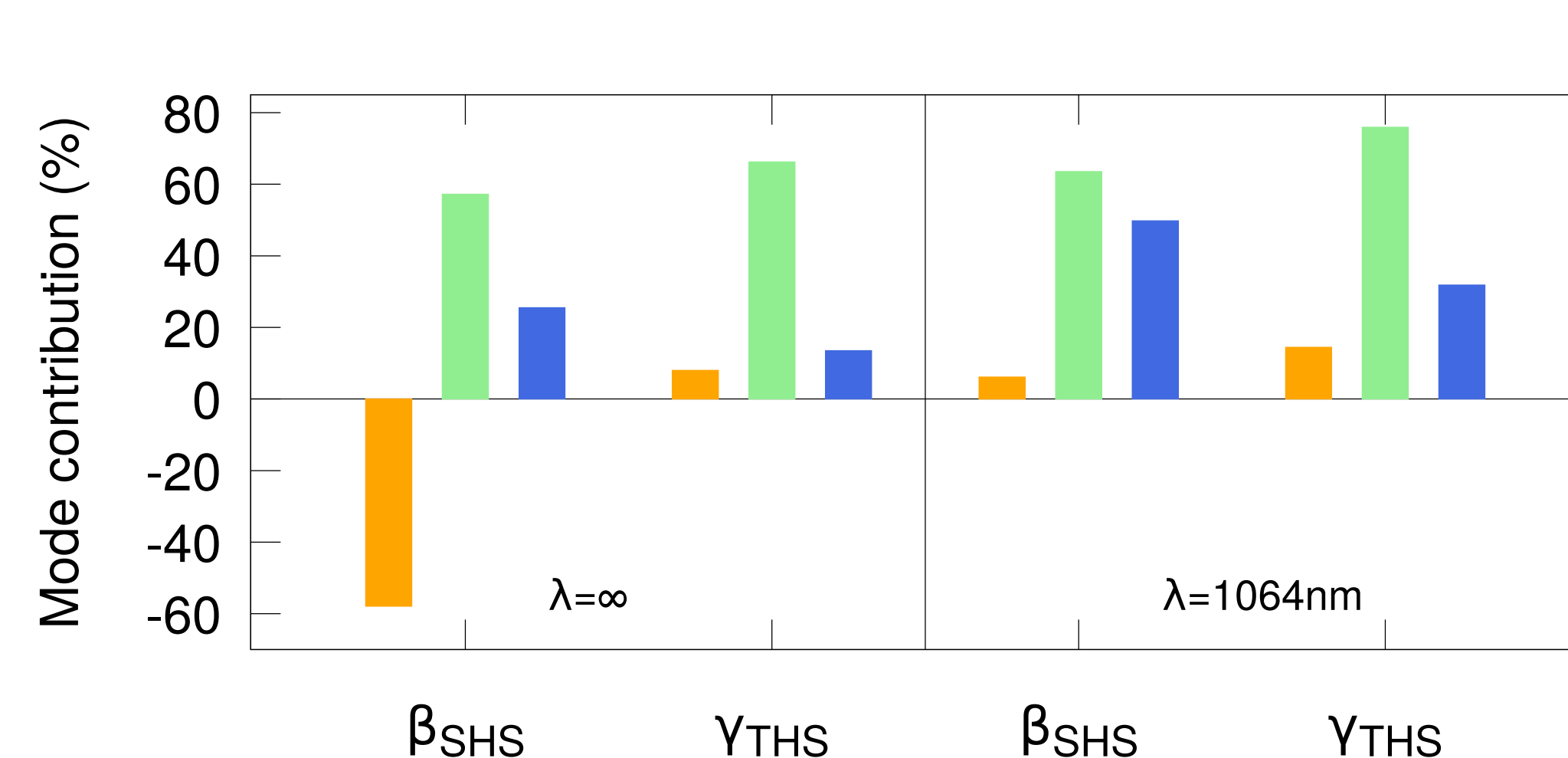
- Contributions of the different parts and frequency dispersion, at the CCSD/d-aug-cc-pVTZ level (missing contribution analysis):

		β_{SHS}				DR_{SHS}			
		P^e	ΔP^{ZPVA}	P^{pv}	P^{tot}	P^e	ΔP^{ZPVA}	P^{pv}	P^{tot}
static		11.04	7.6%	-24.2%	9.49 (-16%)	7.73	-2.3%	0.7%	7.55 (-2%)
1064 nm		11.93	6.4%	3.2%	13.19 (9%)	8.21	-2.8%	-2.6%	7.76 (-6%)

		γ_{THS}				DR_{THS}			
		P^e	ΔP^{ZPVA}	P^{pv}	P^{tot}	P^e	ΔP^{ZPVA}	P^{pv}	P^{tot}
static		1821	3.5%	9.8%	2101 (13%)	76	6.3%	50.7%	166 (54%)
1064 nm		2288	4.4%	-0.2%	2387 (4%)	49	4.8%	-1.1%	51 (4%)

The pure vibrational contribution is large in the static limit, but its frequency dispersion $\propto (\omega_a^2 - \omega_i^2)^{-1}$: it tends to zero for large ω_i . The ZPVA contribution remains important. Altogether, the vibrational contributions are **small, but not negligible** and nonsystematic.

- Impact of the normal modes (missing mode analysis):



Stretching (A_1 and B_2) modes are of first importance, due to a large cubic force constants. Bending mode (A_1) only interesting for static β^{pv} .

Outlook

The amplitude of the vibrational contributions on other reference molecules still need to be investigated. We also would like to check the impact of solvation on γ_{THS} (which is expected to be smaller than on β_{SHS}).

Acknowledgements

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